REVERSE PHASE LIQUID CHROMATOGRAPHY
OF COAL LIQUEFACTION SOLVENTS

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INTRODUCTION

In the various processes for the direct liquefaction of coal a liquefaction solvent is employed which consists, at least in part, of a distillate boiling in the 200 x 500°C range. The composition of this material can have a significant effect upon process performance[1,2]. In our work with SRC-I and H-Coal recycle oils[2,3], we found it desirable to have a method for separating these distillates into component classes which can be quantified to provide a compositional analysis of the material, in a manner similar to the SESC technique[4]. Group separations of this kind have been reported[5,6] using silica or alumina columns with some sequence of solvents of increasing polarity. We felt that the chromatography of these recycle solvents on an ODS reverse phase column might be advantageous in avoiding the problems of irreversible absorption, low selectivity, and alteration of the sample which can occur with the absorption column. The binary gradient used with the ODS column offered much greater flexibility in terms of solvent programming to tailor the separation to a specific type of sample, than was available with the absorption method.

Results are presented on the RPLC separation of Wilsonville SRC-I solvents. These data are quantified and the relative amounts of the eluted fractions provide an explanation of the relative values of these solvents as liquefaction media. Results are also presented on the RPLC separation of H-Coal recycle distillates. It was found that, for the RPLC elution program used, a strong linear correlation exists between the retention time of the component and a "structural vector" consisting of ten parameters which describe that component's molecular structure. This allows one to predict the retention time of a component of interest for qualitative identification, and can also be used to support the identification of a component observed to elute at a given retention time.

EXPERIMENTAL

Separation of Wilsonville Solvents

The Wilsonville solvents were separated using a 25 cm x 6.35 mm ODS column from Lyon Technology. The sample was eluted from the column using a step-wise methanol/water gradient indicated at the top of the chromatogram in Figure 1. Eluted fractions were quantified using a Pye-Unicam moving wire flame ionization detector, and component identifications were made by GC/MS analyses of each fraction. The elutant flow rate was 1.5 ml/min. The chromatogram was divided into twelve more-or-less arbitrary fractions, the fraction cutpoints corresponding to minima in the chromatogram.

Separation of H-Coal Samples

The H-Coal recycle distillates were separated on an Altex C-18 Ultrasphere ODS column (25 cm x 4.6 ml). As above, fractions were quantified usind the Pye-Unicam FID. The elutant flow rate was 1.0 ml/min, and the elution sequence is shown in Figure 2. A 2 min gradient was programmed for each step change in solvent strength. Twenty-eight fractions collected from the RPLC separation of the H-Coal samples,

as indicated in Figure 2, were analyzed by GC/MS to make component identifications. Note that for both separations, the final fraction was removed by a tetrahydrofuran (THF) flush.

RESULTS AND DISCUSSION

Wilsonville SRC-I Solvents

In the course of a program on short residence time liquefaction done under EPRI sponsorship[2] we received relatively large and representative samples of Wilsonville SRC-I recycle distillates over a period of fourteen months. The first sample, Batch I, was hydrogenated in a fixed-bed unit to produce a solvent identified as Hydro II. These were found to be acceptable solvents for bench-scale short residence time liquefaction work. The later batches, Batch III and VI, were found to be unacceptable for use in the continuous short residence time bench-scale unit. The results of this work have been presented in considerable detail elsewhere[2]. For the present purposes it is sufficient to note that Batch I and Hydro II solvents were significantly superior to Batch III and VI solvents in terms of their ability to act as hydrogen donor liquefaction solvents.

The reverse phase liquid chromatogram of Hydro II solvent is shown in Figure 1. Table 1 lists representative compounds in each of the twelve fractions and the approximate weight percentage of each fraction as determined by the FID detector response. Because of the high resolution of the commercial ODS columns used in this study, there was essentially no overlap of components even between two adjacent fractions. Therefore, the functional components occur primarily in fractions 1 through 5, the nonfunctional aromatics in fractions 6 through 11 and the saturated hydrocarbons exclusively in fraction 12. Note also that the sequence of diaromatics (e.g., fluorenes, naphthalenes, dibenzofurans) begins around fraction 5 and each successive fraction contains the next alkylated homologue. Phenanthrene elutes in fraction 7 and pyrene in fraction 8 and again the alkylated homologues appear in order in successive fractions. Hydroaromatics appear earlier than alkyl substituted molecules with the same number of saturated carbons. Thus, dihydrophenanthrene elutes with the methylphenanthrene in fraction 8, and tetra and octahydrophenanthrene in the next two fractions. Fraction 11 contains very highly alkylated aromatics (e.g., C_7 through C_9 naphthalenes).

The RPLC data show a steady increase in the amount of hetero molecules (principally phenols and indanols) upon going from Batch I to Batch VI solvent. Taking fractions 1 through 4 as a group, polar molecules increased from 15.8% (Batch I) to 20.0% (Batch III) to 27.1% (Batch VI). Hydrogenation of Batch I decreased the polar fractions to 10.0% (Hydro II). At the other end of the chromatogram, the saturates approximately double on going from Batch I to Batch VI. Hydrogenation of Batch I increases the saturates by about 50%. The hydroaromatic hydrogen donor molecules are found principally in fractions 7 through 10. Batch III and Batch VI solvents are depleted in these fractions relative to Batch I and Hydro II.

The RPLC data on the Wilsonville recycle solvents can be readily related to the quality of these solvents as hydrogen donors. The Batch I and Hydro II solvents are richer in those fractions which contain the partially hydrogenated aromatics which can serve as hydrogen donors. In Batch III and Batch VI these fractions are displaced by the monoaromatic phenols and indanols and also by saturated hydrocarbons. The more alkylated Batch III and Batch VI solvents are, therefore, expected to be both poorer hydrogen donors and poorer physical solvents than Batch I or Hydro II.

RPLC Separation of H-Coal Recycle Distillate

Figure 2 shows the RPLC chromatogram of a distillate recycle sample from Run 9 of the H-Coal PDU, operated by HRI in Trenton, New Jersey. This chromatogram was obtained as part of a program to analyze recycle oils in the H-Coal process and more

complete details are reported elsewhere([3,7,8]). The elution gradient used is shown at the top of Figure 2. Because a better column was used for the H-Coal distillate, the chromatogram shows higher resolution and was divided into 28 fractions as opposed to the 12 used for the Wilsonville solvent. The purpose of this was to obtain a better qualitative identification by GC/MS of the components in the H-Coal samples. We have found that these components elute in a predictable manner based on a set of standard parameters (i.e., "structural vectors") which define the molecule. By correlating retention times with vectors which describe the molecules we can support identifications and predict the fraction which a given component will elute. In all, we obtained mass spectra for over 500 components of the H-Coal distillate. Grouping isomers as individual components, this list is reduced to 153 entries. Components are represented as structural vectors for correlation with retention times. The ten categories used for structural components are shown in Table 2. We believe the listing in Table 2 is the minimum number of parameters necessary to specify each component to the extent that the GC retention times and mass spectra allow identification. That is, higher level parameters such as points of alkyl substitution cannot be derived for all components from the GC/MS data, and are therefore excluded.

Table 3 gives the tentative identifications of 153 components which were correlated on the basis of structural parameters, with retention times in the RPLC run. The percentage of each fraction in the RPLC chromatogram of the mixture was determined from the integrated response of the Pye-Unicam moving wire FID. The relative amounts of each component in a given fraction were determined from the total ion chromatograms of the GC/MS runs used for component identifications. In most cases the sum of the percentages of the components in a given fraction does not equal 100. This is because: (1) some fractions contained unidentified components which were not used in the correlation, and (2) some of the gas chromatograms were of poor quality because of the small sample size available and accurate quantitation was not possible. The percentages of components in a given fraction do allow a distinction between major and minor components, and, for those components which were found in more than one fraction, show in which fraction the majority of that component elutes. The RPLC eluate was collected in 28 fractions and the mean retention time of each fraction used in the linear multiple regression correlation. The correlation coefficient is 0.988 and the slope of the observed versus calculated retention times is 0.976. No usable GC/MS data were obtained for fractions 1, 2 and 27. Fraction 28, which is eluted with THF, contains naphthenes and normal and branched alkanes from C_{14} through about C_{35}. The average error in the correlation is 2.5 min. Since the average fraction width is over 4 min, and the mean retention times were used for each component in a given fraction, we have an inherent error of $\pm \sim 2$ minutes in the observed retention times.

The calculated retention time coefficients are given in Table 2. Factors which increase molecular size (number of aromatic rings, aliphatic and hydroaromatic carbons) increase the retention time. Parameters which reduce molecular size (aromatic condensation, hydroaromatic rings) decrease retention time.

Hydroxyls and basic and non-basic nitrogens have strong negative correlations. Surprisingly, etheric oxygen has a positive correlation coefficient. However, since only two ethers, dibenzofurans, were detected this parameter is uncertain.

That such a strong linear correlation exists between retention times and the structural parameters is surprising. It is clearly dependent on the solvent program used in the RPLC run. However, we have developed similar correlations for different solvent programs and samples other than H-Coal liquids. Therefore, we conclude that this solvent program is not unique. This suggests that a different program may produce a predictable separation which may have specific advantages for the problem at hand. One use of this method is as a pre-separation when the intent is to detect a specific component. The approximate retention time can be calculated for a given

component, and a fraction of the RPLC eluate can be taken which covers this reten-
tion time. This fraction can then be analyzed, probably by GC/MS, to determine if
the component is present. This will eliminate the interferences in the GC from
structurally dissimilar components with similar GC retention times. This method
also allows concentration of the sample to improve sensitivity.

CONCLUSIONS

Reverse phase liquid chromatography is a promising method for analytical or
preparative separation of coal derived distillates. The high resolution and selec-
tivity of commercially available ODS columns allows specific component classes (e.g.,
polars, aromatics, saturates) to be separated without cross contamination. A wide
variety of elution programs is readily available. The inertness of the column sub-
strate should minimize problems of irreversible adsorption and chemical alteration
of sample components on the column. The rather unexpected result that retention
time can be accurately predicted on the basis of a simple structural representation
of a component opens up interesting possibilities for refinement and application of
the method.

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Table 1

Reverse Phase Liquid Chromatographic
Separation of Wilsonville Solvents

		Wilsonville Batch,[*] approximate, wt %			
Fraction	Representative Compounds	I	II	VI	Hydro II
1	phenol, cresols	0.9	1.0	0.7	0.1
2	quinoline, indole, indanol, xylenols	2.2	2.1	4.7	1.1
3	methyl indanols, C_3-phenols, methyl quinoline	4.4	6.7	9.0	2.3
4	carbazole, C_4 + C_5-phenols, C_6-indanols	8.3	10.2	12.7	6.5
5	methyl carbazoles, diphenylether, C_2-quinolines, naphthalene	8.3	8.2	8.6	7.9
6	dibenzothiophene, dibenzofuran, C_2-carbazole, fluorene, acenaphthene, methylnaphthalene, biphenyl, tetralin	2.5	5.5	2.0	1.3
7	methyl fluorene, C_2-naphthalene, C_1-tetralin, phenanthrene	14.2	12.2	6.7	13.8
8	C_1-phenanthrene, C_3-naphthalene, pyrene, di-hydrophenanthrene	11.7	4.6	6.5	9.4
9	tetrahydrophenanthrene, phenyl naphthalene, C_3-naphthalene, C_2-phenanthrene, C_2-biphenyl	7.0	6.2	5.6	4.2
10	octahydrophenanthrene, C_4 + C_5-naphthalenes, C_1 + C_2-tetrahydroacenpahthenes, C_1-phenyl naphthalene, C_3-biphenyl, C_3 + C_4-tetralins	30.3	28.9	21.7	37.2
11	highly alkylated aromatics	3.2	2.5	7.2	5.1
12	saturated hydrocarbons	7.1	11.8	14.6	10.9

[*] FID detector response

Table 2

Structural Parameters and Coefficients for Reverse Phase
Liquid Chromatogram of H-Coal Hydroclone Overflow Distillate

Structural Factor (X_i)	Coefficient, min, (C_i)
Constant	-10.45
Number of Aromatic Rings	24.28
Degree of Condensation	-5.35
Number of 6-Membered Saturated Rings	-3.80
Number of 5-Membered Saturated Rings	-4.86
Number of Alkyl Carbons	8.78
Number of Naphthenic Carbons	8.79
Number of Hydroxyl Groups	-25.26
Number of Ether Oxygens	11.53
Number of Non-Basic Nitrogens	-11.23
Number of Basic Nitrogens	-28.53

$$\text{Retention Time} = \sum_i C_i X_i$$

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Table 3. Component Identifications – RPLC Separation of H-Coal
Hydroclone Overflow Distillate – PDU Run 9 – Period 20

Fraction	% of Total	Component	% of Component in Fraction	Calc. Retention Time, min	Fraction Mean Retention Time, min	Δ, min
3	1.1	C_2-Phenol	48	6.1	10.2	4.1
		Indole	2	9.9		0.4
		Indanol	47	10.0		0.2
4	1.5	C_3-Phenol	34	14.9	16.3	1.4
		C_1-Indanol	58	18.8		-2.5
		C_2-Quinoline	2	21.8		-5.5
		Phenylphenol	2	12.9		3.4
5	1.0	C_4-Phenol	20	23.7	21.8	-1.9
		C_1-Phenylphenol	5	21.6		-0.1
		C_2-Indanol	21	27.6		-5.8
		C_1-Indole	2	18.7		3.1
		Carbazole	18	22.0		-0.3
6	1.6	C_4-Phenol	10	23.7	25.4	1.7
		C_2-Indanol	40	27.6		-2.2
		C_1-Phenylphenol	5	21.6		3.7
7	1.9	C_5-Phenol	21	32.4	30.0	-2.4
		C_3-Indanol	13	36.4		-6.4
		C_2-Phenylphenol	5	30.4		-0.4
		C_1-Carbazole	20	30.8		-0.8
8	2.2	C_5-Phenol	1	32.4	36.7	4.3
		C_1-Phenol	6	41.3		-4.5
		C_3-Indanol	11	36.4		0.4
		C_4-Quinoline	2	39.3		-2.6
		C_1-Acridine	3	31.9		4.8
		C_2-Carbazole	1	39.6		-2.8
		C_2-Acridine	10	40.7		-4.0
9	2.7	C_6-Phenol	1	41.2	44.1	2.9
		C_4-Indanol	5	45.1		-1.0
		C_2-Carbazole	21	39.6		4.6
		C_2-Acridine	2	40.7		3.4
		C_1-Azapyrene	12	40.2		3.9
		C_3-Phenylphenol	12	39.2		4.9
10	4.1	C_2-Naphthalene	16	50.3	49.4	-1.0
		Acenaphthene	5	45.5		3.9
		Fluorene	25	42.0		7.3
		Dihydroanthracene	1	51.9		-2.5
		Phenanthrene	35	51.7		-2.3
		C_3-Carbazole	1	48.3		1.0
11	2.7	C_2-Naphthalene	1	50.3	52.2	1.8
		C_1-Acenaphthene	2	54.2		-2.1
		C_1-Fluorene	10	50.8		1.4
		Dihydrophenenathrene	6	51.9		-0.3
		Phenanthrene	2	51.7		0.5
		C_1-Dibenzofuran	1	53.6		-1.4
		Benzindan	70	54.2		-2.1
12	2.8	C_1-Tetralin	1	53.9	55.0	1.0
		Tetrahydroacenaphthene	1	57.8		-2.9
		C_3-Naphthalene	15	59.1		-4.1
		C_1-Fluorene	20	50.8		4.2
		C_1-Phenanthrene	7	60.5		-5.5
		Cyclopenta (d,e,f) Phenanthrene	2	55.6		0.7
		Fluoranthene	7	52.2		2.8
		Pyrene	1	59.9		-5.0
		C_1-Dibenzofuran	1	53.6		1.4
		C_4-Carbazole	2	57.1		-2.2
		C_2-Biphenyl	1	55.7		-0.7
		C_1-Acenaphthene	30	54.2		0.7

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Table 3. (continued)

Fraction	% of Total	Component	% of Component in Fraction	Calc. Retention Time, min	Fraction Mean Retention Time, min	Δ, min
13	5.5	C_3-Naphthalene	2	59.1	58.4	-0.7
		Pyrene	28	59.9		-1.6
		C_1-Phenanthrene	38	60.5		-2.1
		Phenylnaphthalene	6	57.0		1.3
		C_1-Fluorene	3	50.8		7.6
		C_2-Fluorene	8	59.6		-1.2
		C_2-Biphenyl	5	55.7		2.7
14	1.2	Dihydropyrene	33	65.5	60.6	-4.8
		C_1-Phenanthrene	9	60.5		0.2
		C_1-Dihydrophenanthrene	5	60.6		0.0
		C_2-Acenaphthene	7	63.0		-2.4
		C_1-Benzindan	3	63.0		-2.4
		C_3-Biphenyl	1	64.4		-3.8
15	4.6	Tetrahydrophenanthrene	21	64.1	62.9	-1.2
		Acephenanthrene	9	64.4		-1.5
		C_4-Naphthalene	3	67.9		-4.9
		C_2-Tetralin	1	62.7		0.2
		C_1-Dihydrophenanthrene	8	60.6		2.3
		C_2-Fluorene	6	59.6		3.3
		C_1-Tetrahydroacenaphthene	1	66.6		-3.7
		C_1-Fluoranthene	1	61.0		2.0
		C_5-Carbazole	1	65.9		-3.0
		C_1-Phenanthrene	1	60.5		2.4
		Tetrahydropyrene	1	65.6		-2.7
		C_3-Biphenyl	4	64.4		-1.5
		C_2-Acenaphthene	22	63.0		-0.1
		Tetrahydrofluoranthene	1	64.6		-1.6
		C_1-Benzindan	13	63.0		-0.1
16	5.0	C_4-Naphthalene	1	67.9	66.5	-1.4
		C_2-Phenanthrene	31	69.3		-2.8
		C_1-Pyrene	24	68.7		-2.2
		Chrysene	3	70.6		-4.2
		Acephenanthrene	3	64.4		2.1
		Tetrahydrocyclopenta (d,e,f) Phenanthrene	1	68.0		-1.5
		C_2-Fluorene	11	59.6		6.9
		C_1-Benzindan	5	63.0		3.5
		C_2-Dihydrophenanthrene	4	69.4		-2.9
17	2.5	C_2-Phenanthrene	23	69.3	69.1	-0.1
		C_1-Dihydropyrene	12	74.2		-5.1
		C_1-Pyrene	30	68.7		0.4
		Chrysene	1	70.6		-1.5
		C_1-Tetrahydrophenanthrene	1	72.9		-3.7
		C_2-Benzindan	3	71.8		-2.7
		Tetrahydrocyclopenta (d,e,f) Phenanthrene	7	68.0		1.1
		C_4-Biphenyl	6	73.2		-4.1
		C_3-Fluorene	4	68.4		0.8
		C_2-Dihydrophenanthrene	1	69.4		-0.3
18	2.1	C_1-Pyrene	40	68.7	70.6	1.9
		C_2-Phenanthrene	20	69.3		1.3
		C_1-Tetrahydropyrene	4	74.4		-3.8
		C_1-Chrysene	1	79.4		-8.8
		C_2-Fluoranthene	4	69.4		0.9

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Table 3. (continued)

| Fraction	% of Total	Component	% of Component in Fraction	Calc. Retention Time, min	Fraction Mean Retention Time, min	Δ, min
19	5.5	C_3-Tetralin	1	71.5	73.8	2.4
		C_5-Naphthalene	4	76.6		-2.8
		C_3-Phenanthrene	8	78.0		-4.2
		C_2-Pyrene	1	77.5		-3.7
		C_1-Dihydropyrene	8	74.2		-0.4
		C_2-Phenylnaphthalene	1	74.6		-0.8
		C_2-Tetrahydroacenaphthene	1	75.4		-1.5
		C_1-Tetrahydrobenzindan		72.9		1.0
		C_2-Tetrahydrophenanthrene		75.4		-1.6
		C_3-Acenaphthene		71.8		2.1
20	7.6	Octahydrophenanthrene	1	76.5	79.0	2.6
		C_5-Naphthalene	4	76.6		2.4
		C_3-Phenanthrene	15	78.0		1.0
		C_2-Pyrene	14	77.5		1.5
		C_1-Chrysene	2	79.4		-0.4
		Benzpyrene	1	78.9		-0.1
		C_2-Dihydropyrene		83.0		-4.0
		C_1-Dihydropyrene	7	74.2		4.8
		C_4-Acenaphthene		80.6		-1.5
		C_2-Tetrahydrophenanthrene		81.6		-2.6
21	3.0	Tetrahydrochrysene	5	83.0	83.7	0.7
		C_4-Chrysene	8	79.4		4.3
		Benzpyrene	1	78.9		4.8
		C_6-Naphthalene	1	85.4		-1.7
		C_3-Phenanthrene	14	78.0		5.7
		C_4-Tetralin	1	80.2		3.5
		Dihydrobenzpyrene	1	84.4		-0.7
22	2.1	C_4-Phenanthrene	21	86.8	87.1	0.3
		C_3-Pyrene	11	86.3		0.8
		C_2-Chrysene	2	88.2		-1.1
23	2.7	Benzchrysene	1	89.6	90.4	0.8
		C_3-Pyrene	19	86.3		4.1
		C_4-Phenanthrene	8	86.8		3.6
24	3.0	C_5-Tetralin	8	89.0	94.4	5.4
		C_1-Octahydrophenanthrene	7	85.2		9.2
		C_5-Phenanthrene	5	95.6		-1.2
		C_6-Tetralin	2	97.8		-3.4
25	5.5	C_6-Tetralin	5	97.8	99.0	1.2
		C_3-Octahydrophenanthrene	9	94.0		5.0
		C_5-Phenanthrene	11	95.6		3.5
		C_4-Pyrene	7	95.0		4.0
26	6.5	C_6-Phenanthrene	2	104.4	106.6	2.3
		C_5-Pyrene	11	103.8		2.8
27	10.2	No Components Identified				
28	11.0	Alkanes and Naphthenes				

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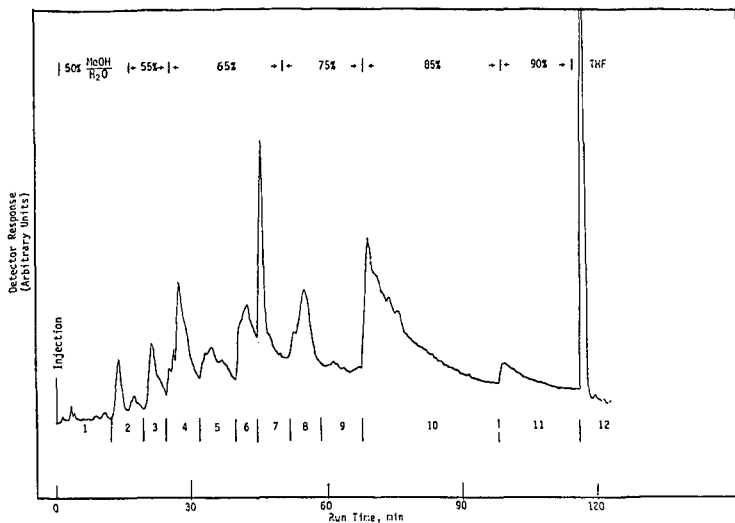
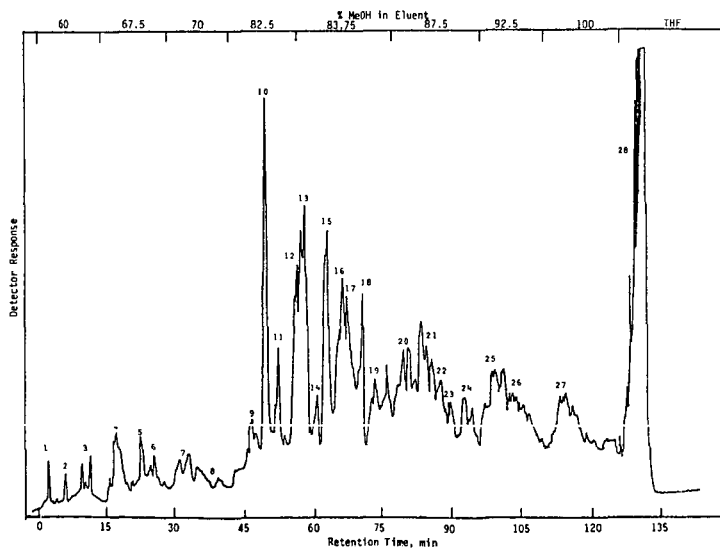Figure 1.   RPLC of Wilsonville Hydro II SRC-I Solvent

Figure 2.   RPLC of H-Coal Hydroclone Overflow Distillate (Period 20 - PDU Run 9)

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